DOE/PC/88924--12

DE92 002760

DOE/PC/88924-12

Thermodynamics of the Solvent Swelling of Coal

Technical Progress Report #12

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For the Period June 1 to August 31, 1991

This report was prepared with the support of the U.S. Department of Energy, Grant No. DE-FG22-88PC88924. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author and do not necessarily reflect the views of DOE.

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ABSTRACT

Sorption of benzene by the pyridine-extracts of premium Argonne Illinois #6 coal was studied at several relative vapor pressures at 50°C and 70°C. The amount of benzene sorbed by the extract increases linearly or nearly linearly with benzene vapor pressure. The extrapolated lines do not pass through the origin. At low pressures, a dual-mode sorption mechanism is proposed, whereby benzene concurrently fills holes (microvoids) and dissolves into the extract. At higher pressures, we propose that the holes are saturated and that only dissolution is occurring. Dissolution thus increases linearly with pressure of benzene. The heat of dilution, calculated from the change in slope of the curve with temperature, is positive, indicating an endothermic process. This result is in distinct contrast to results obtained previously using pyridine as solvent.

The O-methylated extract absorbs considerably more benzene at 50°C compared to the extract. Again, the sorption curve is linearly, with a slope 1.5 times that of the extract. The increase in slope is consistent with the disruption of hydrogen bonds by O-methylation.

INTRODUCTION

The principal goal of this research is to develop an understanding of the thermodynamics of the swelling of coals in various solvents. The approach is unique in the sense that the uncrosslinked portion of the coal is being swollen, as opposed to the crosslinked portion. This approach avoids complications due to the crosslinked nature of coals, and allows the experimental data to be interpreted in terms of modern theories developed for polymer solutions.

We are currently working with the pyridine-extract of Argonne premium Illinois No. 6 coal. The extract was exposed to benzene at several relative pressures and 50°C and 70°C and the equilibrium weight of benzene was measured. The amount of benzene sorbed increases linearly with pressure for both the extract and O-methylated extract. The extrapolated line yields a nonzero, positive intercept. We interpret this intercept as the total amount of pyridine that fills holes or microvoids in the extract. If this interpretation is correct, it indicates that swelling (or dissolution) of the extract increases linearly with benzene pressure (obeys Henry's law). These results are similar to results reported previously using pyridine as the solvent.¹ The heat of dilution calculated from the change in slope of the sorption isotherm at 50 and 70°C is positive, indicating an endothermic process. The result is in distinct contrast to the exothermic heats of dilution reported for the pyridine-Illinois No. 6 extract system.¹

EXPERIMENTAL

Sample preparation

Argonne Premium coals were obtained from Argonne National Laboratory in ampoules of five grams of -100 mesh coal. The coal was first dried under vacuum at 105°C to constant weight and then analyzed for carbon, hydrogen, and nitrogen. Analysis found: Illinois #6; C, 65.57; H, 4.66; N, 1.24.

Approximately 4.5 g of the sample was Soxhlet-extracted with dry pyridine under argon for several days until the siphon liquid was clear. The pyridine solution was then filtered through a 0.4 μ m nylon membrane filter to insure removal of particulates and colloidal material. The filter did not plug. Most of the pyridine was removed by rotovaporization under reduced pressure at 70-80°C. Approximately 200 mL of a methanol/water (80/20 vol.) mixture and 2 mL of conc. HCl were added to the flask and the mixture was stirred under nitrogen for two days. The solid extract was then filtered and dried under vacuum at 105°C for 24 hours. The extractability was 27.2% (wt.) for Illinois #6.

Sorption Experiments

Sorption experiments using benzene as solvent were carried out using a quartz spring balance shown in Figure 1. The balance consists of a quartz spring, a large 5 liter flask, vacuum inlet system, and MKS pressure transducer (0-1000 torr, 0.5% accuracy). The entire balance chamber, including transducer, is housed in a Precision Scientific circulating (forced air) drying oven, which is maintained at a constant temperature by a I²R thermowatch temperature regulator which activates a light bulb.

Figure 1. Sorption Apparatus

The sample is suspended from the quartz spring and, as the sample sorbs solvent, the spring extends until equilibrium is reached. The extension of the spring is measured through a window on the door of the oven using a sensitive Eberbach cathetometer (travelling telescope). The spring is calibrated at the appropriate temperature using standard weights before the experiment is conducted. The experiment, thus, allows determination of the mass of solvent sorbed by the sample at a given partial pressure and temperature. The purpose of the 5 liter flask to minimize pressure changes caused by sorption of solvent by the sample. Quartz springs of the type used here have a linear-extension versus suspended-weight relationship and exhibit no hysteresis within the range of weights for which the spring is designed.

The experimental procedure was as follows. Approximately 50 mg of extract was placed in the quartz bucket and weighed on an electronic balance. The bucket and sample were then suspended on the spring. The hangdown tube was replaced and the system was evacuated to less than 0.1 torr and brought to the appropriate temperature ($50 \pm 0.02^{\circ}\text{C}$). The system was allowed to evacuate overnight. Purified benzene was placed in the round bottom flask shown in Figure 1 and frozen with dry ice/isopropanol. Stopcock B was closed, and stopcock C was opened to evacuate air from the flask. Then stopcock C was closed, and the pyridine was thawed and refrozen. Stopcock C was again reopened for evacuation. This procedure insures removal of last traces of air. Stopcock A was closed and stopcocks B and C were then opened until the appropriate pressure of benzene was reached. After equilibrium was achieved, the pressure of benzene was again raised. This procedure was repeated until the entire pressure range was covered.

RESULTS AND DISCUSSION

The pyridine-extract of the Illinois No. 6 coal was exposed to benzene at various vapor pressures at 50 and 70°C. Several incremental sorption experiments were conducted in that, once equilibrium was attained at a particular pressure, the pressure was raised and the system was again allowed to attain equilibrium. The equilibrium amounts of benzene sorbed by the extracts are plotted against relative pressure of benzene in Figure 2. Note that there is a reasonably good straight-line correlation between sorption values and pressure. The curves drawn are least-squares fits. In each case the correlation coefficient was 0.98 or better.

The results in Figure 2 demonstrate that sorption of benzene by the extracts obeys Henry's Law, i.e., the solubility of benzene in the extract increases linearly with pressure. However, the curves do not pass through the origin. This result is similar to those of Michaels *et al.*, who observed that the solubilities of several gases in polyethylene terephthalate obeyed Henry's Law.² For two of the gases, carbon dioxide and ethane, the sorption isotherms were curved at low pressures but linear at higher pressures. They interpreted their results by proposing that sorption took place by two concurrent mechanisms at the lower pressures; ordinary dissolution and "hole-filling." At higher pressure, the holes or microvoids were saturated with only dissolution occurring. The intercept was interpreted as the total amount of sorption due to filling of the microvoids. Thus, a quantitative separation of the two processes was possible.

Following the work of Michaels *et al.*,² we suggest that the intercepts observed in Figure 2 represent the total amount of benzene that fills holes in the extracts. We provided a similar interpretation for the sorption results with pyridine.¹ If this interpretation is correct, it indicates that the holes are

Figure 2. Sorption Isotherm for Pyridine-extract of Illinois No. 6 Coal and Benzene.

saturated at a relative pressure of 0.2 and that only dissolution of benzene in the extract is occurring at this pressure and higher.

Solubility constants can be calculated from the data shown in Figure 2. The solubility constant, K_p is simply the slope of the straight-line portion of the curve. The solubility constants are given in Table I. The constants show that the solubility of benzene in the extract increases slightly with temperature.

TABLE I
Solubility Constants and Heats of
Dilution for Extract-Pyridine Systems

Solvent	K_p , mg/g(p/p) ^a		ΔH_{dil} , kcal/mol
	50°C	70°C	
Benzene	143	157	+1.0
Pyridine	395 (396)	331 (332)	-2.0

^aNumber in parentheses represents duplicate experiment.

Heats of dilution were calculated from the sorption data using the following equation.

$$\Delta H_{dil} = -RT^2 \ln (K_{p1}/K_{p2})$$

where K_{p1} and K_{p2} are the solubility constants at 50°C and 70°C, respectively. The results are summarized in Table I. Note that benzene yields a positive heat of dilution indicating a net endothermic interaction, in contrast to results with pyridine, which show a negative heat of dilution.

The data in Table I indicates that pyridine is about 2.8 times more soluble

in the extract than benzene at 50°C. We argue that this ratio of quite reasonable. For example, Larsen et al., using a volumetric method, determined that the pyridine-insoluble Illinois No. 6 coal absorbed were 2.6 times more pyridine than benzene (by volume) at ambient temperature.³ On a weight basis, this corresponds to a ratio of 2.9 (pyridine:benzene). Although this ratio is for the insoluble coal (not the extract) and at ambient temperature (not 50°C), we believe it lends credence to our interpretation that the slope of the isotherms represents solubility.

Finally, we determined the solubility constant of the O-methylated Illinois No. 6 pyridine-extract to be near 205 (two determinations) at 50°C. This indicates that benzene is 1.4 times more soluble in the O-methylated extract than the extract. Larsen et al., using the volumetric method, determined that the O-methylated Illinois No. 6 coal absorbed 1.4 times more benzene than the pyridine-extracted Illinois No. 6 coal.³ Our results are entirely consistent with theirs.

FURTHER WORK

The project officially ended on August 31, 1991. We are finishing final experiments with benzene as solvent and will report all results in the Final Report to be submitted by November 30, 1991.

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